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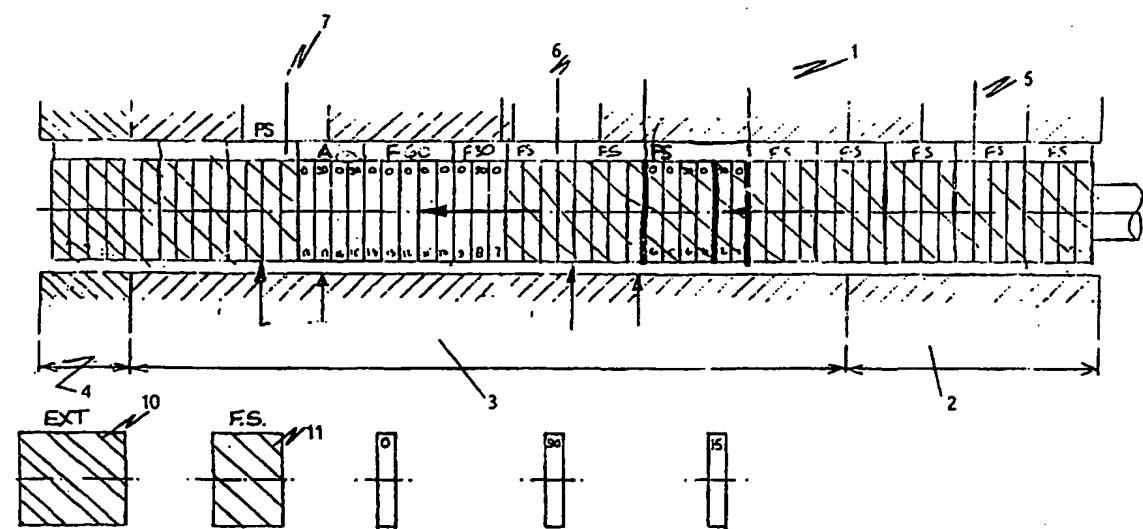
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/IE96/00060 <b>(22) International Filing Date:</b> 6 September 1996 (06.09.96) <b>(30) Priority Data:</b> S950699                      8 September 1995 (08.09.95)                      IE <b>(71) Applicant (for all designated States except US):</b> SOLPLAX LIMITED [IE/IE]; Wood Quay Court, Wood Quay, Galway (IE). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> GILTSOFF, Bayan, Oleg, Thadius [IE/IE]; Jemeela, Killgobin Lane, Stepside, County Dublin (IE). <b>(74) Agent:</b> MACLACHLAN & DONALDSON; 47 Merrion Square, Dublin 2 (IE).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DE (Utility model), DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> BIODEGRADABLE PLASTIC MATERIAL AND A METHOD FOR ITS MANUFACTURE		
		
<b>(57) Abstract</b> <p>A method of manufacturing a biodegradable plastics material comprising the following steps: (a) mixing a stabiliser with a partially hydrolysed, water-soluble polyvinyl alcohol (PVA) co-polymer; (b) adding a plasticiser to the mixture of stabiliser and PVA; and (c) mixing the PVA, plasticiser and stabiliser at a temperature in the range of between 106 to 140 °C whereby the resultant material can readily be worked by known processes and is suitable for the manufacture of water soluble and biodegradable articles, optionally, after the mixing stage, the method includes the steps of compounding and pelletising the resultant product to produce a useable, commercial pellet wherein the compounding is carried out at a temperature in the range 195 - 225 °C. The method includes processing the plastics material further by blow moulding, cast extrusion, injection moulding or any other suitable type of process currently in use. The invention also discloses an article produced by the above method.</p>		

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## BIODEGRADABLE PLASTIC MATERIAL AND A METHOD FOR ITS MANUFACTURE

5 The present invention relates to a biodegradable plastics material and to a method for its manufacture. In particular, the invention relates to a biodegradable plastics material comprising a polyvinylacetate/polyvinylalcohol copolymer.

10 Commercially available biodegradable plastics do not fully degrade in the environment and retain a high degree of toxicity when partially degraded. Furthermore, such materials are expensive and generally only used for niche markets.

15 The use of polyvinylacetate/polyvinylalcohol (PVA) copolymers for the manufacture of biodegradable plastics materials is described in WO92/01556. By layering or surrounding PVA which is water soluble at 20°C with a thin layer of a PVA which is water insoluble at 20°C, an article which is protected from dissolution by water until its waterproofing, insoluble layer is breached may be manufactured. The  
20 PVA's are co-extruded as a laminate or may be moulded, with or without an intervening filler layer. Water soluble PVA dissolves readily in water and is broken down in the environment within a relatively short time to carbon dioxide and water.

25 German Patent No. 1127085 discloses that in order to process PVA plastics material on standard processing apparatus such as profile extruding machines, blown film extruders or injection moulding machines, undesirable thermal decomposition of the products occurs at temperatures above 150°C and must be prevented by external plasticising of granular  
30 plastics material. The plastics material is plasticized by mixing with a suitable plasticizer for 15-30 mins. at a temperature of up to 110°C. This plasticized PVA can be injection moulded and extruded under the following conditions: heating the material to a temperature in the range 145-190°C and at an injection pressure of 100-130 bar.

35

While PVA is known as a biodegradable material, its use in the

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manufacture of plastic articles has up to now been limited as it is technically difficult to work with this material and to produce an acceptable product, therefore it is costly and commercially unsuccessful.

- 5 The present invention seeks to provide an improved plastics material comprising a PVA copolymer which can readily be worked by known processes such as blow moulding, injection moulding, cast extrusion, etc. and which is suitable for the manufacture of biodegradable articles.
- 10 The term PVA as used herein refers to a polyvinylacetate polymer which has been partially hydrolysed to convert a proportion of the acetate groups to the corresponding alcohol. Therefore, the term refers to a polyvinylacetate/ polyvinylalcohol copolymer. The solubility of the PVA is dependent, *inter alia*, on the degree to which the PVA is hydrolysed.
- 15 "Cold soluble" PVA denotes a copolymer which is generally referred to as "partially hydrolyzed" polyvinylacetate. Typically, the partially hydrolyzed copolymer comprises 70 to 85 wt % of the alcohol, with the remainder comprising residual acetate, and this material is soluble in "cold" water. It is generally readily soluble in water at 20°C. Further
- 20 hydrolysis of the PVA to levels at which the alcohol comprises about 96 mol % or greater (usually referred to as "fully hydrolyzed" polyvinylalcohol, results in a marked decrease in solubility. While the fully hydrolysed polymer is usually thought of as insoluble, it is in fact soluble in water at a temperature of about 50°C or greater. Such
- 25 material is referred to herein as "hot soluble" PVA. Both hot and cold soluble PVA's, once dissolved, are fully biodegradable in nature to CO<sub>2</sub> and H<sub>2</sub>O. The undegraded copolymers and their partially degraded derivatives are non-toxic.
- 30 The present invention provides a method of manufacturing a biodegradable plastics material comprising mixing partially hydrolysed, water soluble polyvinyl alcohol (PVA) co-polymer with a plasticiser and stabiliser at a temperature in the range of between 106 to 140°C, whereby the resultant material can readily be worked by known processes and is suitable for the
- 35 manufacture of water soluble and biodegradable articles.

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The method may comprise the following steps:

- 5 a. mixing the stabiliser with the PVA; and
  - b. adding the plasticiser to the mixture of stabiliser and PVA and mixing at a temperature between 106 to 140°C.
- 10 After the mixing stage, the method may include the steps of compounding and pelletising the resultant product to produce a useable, commercial pellet wherein the compounding is carried out at a temperature in the range 195 - 225°C.
- 15 The method may include processing the plastics material further by blow moulding, cast extrusion, injection moulding or any other suitable type of process currently in use.
- The mixing stage may include mixing PVA and stabiliser are mixed in a forced action blender.
- 20
- The stabiliser may be included in an amount in the range of 4 to 6% w/w (weight of stearamide to weight of PVA) and the plasticiser is included in an amount in the range of 3 to 15% w/w (weight of plasticiser to weight of PVA).
- 25
- The stabiliser may stearamide or a stearate and the plasticiser may comprise glycerol or glycerine solution or soya bean oil.
- 30 The mixing stage may be carried out at a temperature in the range of 123 to 129°C.
- The method may include the step of applying a waterproofing agent to at least a portion of the surface of the plastics material so that at least a portion of the material is rendered resistant to water to prevent premature dissolution of the product on contact with water.
- 35

The waterproofing agent may be phenoxy resin.

- 5 The invention also provides a fully or substantially fully biodegradable article produced by the method of the invention.

According to the invention, the addition of a stabiliser to the PVA feedstock during compounding of the plastics material results in a product which can readily be worked into a product by any of the commonly used methods. The PVA feedstock may be cold or hot soluble, partially hydrolysed PVA which is 70-85 wt % polyvinyl alcohol. A broad range of polymer molecular weights are suitable for use, depending on the desired characteristics of the final product. Generally, molecular weights in the range of 20,000 d to 90,000 d are usable. Plastics made from PVA's falling into the lower part of this range will be softer and pliable, and will be suitable for making relatively flimsy films. Selection of PVA's from the upper end of the range will allow much harder plastics to be made, for example for making articles such as bottles, moulds, bowls, etc. The preferred molecular weight range is from about 50,000 d to about 60,000 d, degree of hydrolysis 76.7-79.3 mol%. PVA's in this range, when compounded as described herein, may readily be extruded to give good quality product.

- 25 The most preferred stabiliser for use in the manufacture of the plastics material is stearamide (octadecanamide), which is a fully biodegradable substance. Alternatively stearates such as zinc stearate can also be used. Stearamide is added in the range of between about 4 to 6 wt %, with 5 wt % being preferred.

- 30 A plasticiser is also added and preferably this will also be a biodegradable substance. Typically, the plasticiser will be glycerol or glycerine and will be present in the range of between about 3 to 15 wt %, preferably 5 to 10 wt % and optimally about 5 wt %. The stearamide and glycerol in combination provide an excellent stabilising/plasticising effect in the plastics material. The rigidity of the plastics product
- 35



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can be controlled by varying the amount of glycerol and stearamide added, the product becoming softer and more pliable as the weight % of stearamide and/or glycerol is increased.

- 5 Other additives, well known in the art, may also be used in compounding the plastics material according to the invention. Such additives may include colouring compounds and fillers.

- 10 The plastics material may be compounded by any suitable means known in the art. Most preferably, the PVA feedstock in the form of powder or granules is mixed with the stearamide, glycerol and optional other ingredients in a forced action blender. However achieved, the mixing will be done at an elevated temperature of between 106 to 140°C, preferably between 123°C and 129°C when film will be blown subsequently, and optimally about 125°C. After mixing, the plastics material may be  
15 pelleted or otherwise prepared, ready for forming into a desired article by extrusion, moulding or otherwise.

- The article prepared in this way will be fully or almost fully  
20 biodegradable. When it is to be discarded to waste, it need only be brought into contact with water, either cold or hot, depending on the PVA feedstock chosen, to cause it to dissolve. The dissolved PVA will then be fully biodegradable within about 28 days to CO<sub>2</sub> and H<sub>2</sub>O. Likewise, the biodegradable additives in the plastics material will degrade. The  
25 PVA in itself is non-toxic and therefore poses no environmental hazard during the time during which it is being biodegraded.

- Clearly, the plastics material described above is suitable only for the manufacture of articles which do not, or are unlikely to, come into  
30 contact with water during their normal usable life. According to another aspect of the invention, a PVA plastics articles which is at least partially waterproof, water resistant or hydrophobic is provided. Water resistance will be required in any article which during its normal storage or use, is in contact with an aqueous environment or a humid  
35 environment. Those surfaces of the article which are exposed to the

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aqueous or humid environment need to be protected from that environment until such time as the article is to be discarded to waste. Examples of such articles include, without limitation, plastic bags, sachets, sacks, wrappers, packaging and the like, films, containers including bottles, jars, beakers, pots and the like and liners including sanitary products such as napkins, nappy liners and the like. Many other applications will suggest themselves to the skilled person. In some cases, all surfaces of the article will require to be rendered waterproof while in other cases, only a portion of the article need be so treated. However waterproofed, the article will easily be disposed of after use. In the case where only a portion of the article has been made water resistant, contacting the untreated portion of the article with water will cause the article as a whole to dissolve. Where all exposed surfaces of the article have been waterproofed, then for disposal, the article need only be broken to expose its interior to the aqueous solvent and thereafter, dissolution of the entire article will occur.

The waterproofing may be achieved in any suitable way or combination of ways, as will now be described.

20

(1) *Polymer Crosslinking.* A thin layer of the surface of the article may be made water resistant by crosslinking the copolymer. One way of achieving this is to add an ultra-violet sensitiser to the PVA during compounding, for example sodium benzoate, benzamide, benzoic acid or tetrazolium salts. After forming an article from the plastics material, the article is subjected to ultra-violet irradiation, during which the sensitiser promotes crosslinking of the polymer chains at the irradiated surface, rendering the crosslinked polymers insoluble, with the effect that a thin layer of the PVA at the surface of the article becomes water resistant. Optionally, a migrating agent may be added to assist the movement of the sensitiser to the surface. Alternatively, the sensitiser may be applied to the surface of the article after manufacture and prior to irradiation.

(2) *Silanisation.* The article or a surface thereof may be coated with

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silane. The silane may be in liquid or gaseous form. The article may be bathed in a silane, or the silane may be applied to the article by dipping, spraying or painting. This is valid for light water resistance.

5

(3) *Treatment with other waterproofing compound.* A waterproofing compound may be added to the PVA feedstock during compounding of the plastics material. This compound may be a hydrophobic substance. A migrating agent may be added to assist movement of the waterproofing compound to the surface of the article formed from the plastics material. The waterproofing agent may itself be a migrating agent. As an alternative to compounding the waterproofing agent into the plastics, it may be applied to the finished article by dipping, spraying or painting. One suitable waterproofing agent is phenoxy resin. Polyvinylacetate or other suitable, non-toxic polymer may be used as a surface coat on the PVA article. To assist adhesion of the waterproofing agent to the surface of the article, it may be treated for example by electrical treatment prior to coating to condition the surface so as to render it more able to accept and retain the waterproofing coating.

20

In some cases, it will be appropriate to manufacture the article from hot soluble PVA. Provided that the article does not encounter water at a temperature in excess of about 45°C during its normal use, such a product need not be surface water-proofed. After use, placing the object in water heated to at least 50°C will promote its dissolution for disposal. An article prepared in this way will be fully or almost fully biodegradable.

30

The invention will now be described more particularly with reference to the following non-restrictive examples and to Figure 1 of the drawings in which is shown an embodiment of the screw design used in the apparatus at the compounding stage of the process of the present invention.

#### Example 1

35

#### Mixing Stage

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A Prism lab 6 high speed mixer was used (Henschel 50kg mixer also used).

### Ingredients

- 5     5kg PVA (degree of hydrolysis of 76.7 to 79.3 mol%)  
0.25 kg stearamide (5% w/w of stearamide to weight of PVA)  
0.25 kg of glycerol (5% w/w of glycerol to weight of PVA)

- 10     A high speed forced action blender was used. The PVA and stearamide were added to the mixer and mixed for 1 minute. The glycerol was added slowly over a period of 30 seconds, with the mixer rotating at approximately 500 rpm. As a result of the agitation, the mix became frothy ("fluffed up") and the mixer was stopped to push mixed material from the inside of the mixer. After 2-5 minutes, the mix had settled down and the mixer was
- 15     turned up to full speed, from 1,500 rpm to 3,000 rpm. As a result of the kinetic energy generated by the agitation of the mix, the temperature increased to 123° and went to 125° in 8 to 20 minutes depending on the type of mixer used.
- 20     The temperature is a critical parameter to achieving high quality product.

- A vacuum was created at the top of the mixer to draw off any moisture vapour which had formed at the top of the mixer and which would otherwise
- 25     condense back into the mix.

- The mix was allowed to cool to 60-70°C so that it was sufficiently cool to allow it to be bagged. The mix can be allowed to cool by itself or optionally a heating/cooling jacket can be included on the mixer vessel.

- 30     Alternatively mix can be transferred to another vessel to cool. The mixture was stirred occasionally to help cooling and break up any lumps which had formed. The product is in granular form and is bagged in air-tight bags.

35

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Compounding/pelleting stage

A Prism TSE 16TC twin screw extruder with 4 1/2mm die was used for the compounding stage.

5

The temperature range was 200°C - 218°C measured from the feed end of the screw to the die end.

The extruder is vented along the screw to allow moisture vapour to exit the screw because otherwise bubbles occur in the strands. The product emerges from the extruder in the form of a strand which has elastic properties. The strands must be dried in air using air knives, for instance, and not in water. After cooling, the strands were cut into pellets using a Prism LPT 16 laboratory pelletiser. The pellets were then bagged in an air tight fashion.

15

The screw design of the twin screw extruder is shown in Figure 1. A single screw apparatus could also be used for compounding.

Referring to Figure 1, the screw is indicated generally by reference numeral 1 and includes three zones, namely a feed zone 2, a work zone 3 and a die zone 4.

20

The feed enters the screw through a feed port 5. Two other ports 6, 7 are included along the length of the screw, to allow for addition of material if required, (6) and for venting (7) respectively. A heating band and a temperature probe respectively are included at two locations along the length of the screw.

25

The configuration of the screw includes several elements namely an extrusion screw indicated by the letters EXT (length = 1.5 times the diameter) and feedscrew elements indicated by the letters FS (length equal to its diameter). The screw also includes mixing elements (length = diameter divided by 4) which may be 0° offset, 90° offset or 15° offset. The mixing elements may be forwarding (F), reversing (R) or

30

35

- 10 -

alternating (A).

Blowing film

5 A Betol 0250 film tower machine was used.

The temperature profile along the screw extruder is as follows:

10 Feed zone of barrel 195-210°C  
Work zone of barrel 200-218°C  
Die zone 200-218°C

15 Screens of 200/inch<sup>2</sup> gauge size are used to soften the memory of the PVA and reduce the risk of any possible extraneous matter and gels. Further screens are also provided of 40/inch<sup>2</sup>, 60/inch<sup>2</sup>, 80/inch<sup>2</sup>, 100/inch<sup>2</sup> and 120/inch<sup>2</sup> secured to the 200/inch<sup>2</sup> screen to give it strength.

Screens are located between the end of the screw and the die.

20 Spraying the waterproofing agent, phenoxy resin, onto the film

Mixing (before spraying)

25 100g phenoxy resin was mixed with 500mls Methyl Ethyl Ketone (MEK) initially to 20% w/w solids. This is mixed in a high speed mixer or is left to stand at a temperature of a minimum of 28°C for 3-5 days with periodic shaking to achieve a solution. When the phenoxy resin was in solution, a mixture comprising 500 mls of MEK and 12mls water was added to the solution. Thus the phenoxy resin was then in solution at a  
30 concentration of approximately 10% w/w.

A 10% w/w solution of phenoxy resin was used for spraying a film of thickness 40 µm. Alternatively 5% or 2.5% solution of phenoxy in MEK with water added was also be used depending on the thickness of the film  
35 to be sprayed. Lower concentrations of phenoxy resin in MEK with water

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may also be used.

### Spraying

5     Spraying was carried out in dry conditions and preferably at a minimum  
temperature of 21°C. A Campbell Hausfeld Professional Turbo Spray (high  
volume/low pressure finishing system HV2,000) was used for spraying but  
conventional sprayers may also be used. The humidity of the atmosphere  
10    in which spraying is being conducted is a critical parameter. The film  
was sprayed so as to achieve good cover but without overspraying. Thin  
film below 40 µm needs stretching so that no folds occur during spraying  
and must be held flat. Heavier plastics must also be held flat.  
Alternatively, heavier plastics (60 µm+) can be dipped or use sponge or  
15    roller to apply.

### Example 2

#### Mixing stage

#### 20    Ingredients

5 kg PVA (degree of Hydrolysis of 76.7 to 79.3 mol %)  
0.5 kg glycerol (10% w/w) glycerol  
0.25 kg (5% w/w) stearamide

25

The procedure is the same as in the mixing stage described in Example 1.

#### Compounding/pelletising stage

30    The temperature profile along the screw extruder was as follows:

Feed zone of barrel 200°C  
Work zone of barrel 205°C  
Die zone                    210°C

35

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Rpm 260

Output 2.5kg/hr approximately

Example 3

5

Mixing stage

5 kgs PVA

0.75 kg glycerol (15%w/w) glycerol

10 0.25 kg (5%w/w) stearamide

Compounding/pelletising stage

Feed zone of barrel 200°C

Work zone of barrel 215°C

15 Die zone 216°C

Rpm 260°

Output 2.5kg/hr approximately.

20 Further Examples of parameters at the compounding and blowing stages

A Prism TSE 16TC apparatus was used for compounding with a blow line attachment for blowing film.

25 The temperature of the various zones is given in °C in the following examples.

Example 4

30	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	215	209	207	200

35 Good quality film was produced.



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Example 5

5		Film			
		Blowing	Die	Work	Feed
		<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
		215	209	209	197
10	Pressure	40-45 bar (4000-4500 kN/M <sup>2</sup> ) (pressure at exit end of screw)			
	Feed	0.5			
	rpm	303			

15 Example 6

		Film			
		Blowing	Die	Work	Feed
		<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
20		215	212	209	199
	Pressure	40-45 bar (4000-4500 kN/M <sup>2</sup> )			
	Torque	7.8 -8.0 NM			
	Rpm	301			

25 Example 7

		Film			
		Blowing	Die	Work	Feed
		<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
30		195	202	191	183
	Pressure	60 bar (6000 kN/M <sup>2</sup> )			
	Torque	8.0-8.4 NM			

35 These parameters resulted in poor quality film.

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Example 8

	Film			
	Blowing	Die	Work	Feed
5	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	188	201	188	182
	Pressure	75 bar (7500 kN/M <sup>2</sup> )		
10	Torque	8.6 NM		

These parameters also resulted in production of poor quality film.

Example 9

15	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	182	202	189	182
20				

These parameters resulted in the production of poor quality film.

Example 10

	Film			
	Blowing	Die	Work	Feed
25	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	192	197	181	176

30 These parameters also resulted in production of poor quality film.

35

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Example 11

	Film			
	Blowing	Die	Work	Feed
5	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	192	191	177	171

It was not possible to produce film at these temperatures.

10

Example 12

	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
15	213	212	208	200

Pressure 45 bar (4500 kN/M<sup>2</sup>)

Rpm 301

20

Good quality film was produced.

Example 13

	Film			
	Blowing	Die	Work	Feed
25	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	214	211	207	200

30 Pressure 40-45 bar (4000-4500 kN/M<sup>2</sup>)

Torque 8-8.5 NM

Feed 0.35

35

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Example 14

	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
5	219	214	215	202

Good quality film was produced.

10 Example 15

	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
15	222	218	216	203

Good quality film was produced.

Example 16

	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
20	225	220	219	204

25

These parameters resulted in borderline quality.

Example 17

	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
30	229	221	221	204

35 Poor quality film was produced.

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Example 18

	Film			
	Blowing	Die	Work	Feed
5	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	228	223	224	205

Poor quality film was produced.

10

Example 19

	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
15	228	226	227	206

Poor quality film was produced.

20 Example 20

	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
25	228	229	231	206

Poor quality film was produced.

Example 21

30	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	228	231	231	206

35

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Poor quality film was produced.

Example 22

	Film			
5	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	238	230	231	206

- 10 It was not possible to blow film from the material exiting the screw extruder at these temperatures.

Example 23

	Film			
15	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	213	210	207	201

- 20 Good quality film was produced.

	Pressure	35-40 bar (3500-4000 kN/M <sup>2</sup> )
	Torque	7.6-8.0 NM
25	Rpm	302

Example 24

	Film			
	Blowing	Die	Work	Feed
30	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	212	211	208	201

Good quality film was produced.

35

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Example 25

	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
5	213	210	204	194

Good quality film was produced.

10	Pressure	40-45 bar (4000-4500 kN/M <sup>2</sup> )
	Torque	7.7-8.2 NM

Example 26

	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
15	213	209	208	194

20 Example 27

	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
25	210	208	202	194

Example 28

	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
30	209	210	204	197

35

- 20 -

Example 29Ingredients

- 5      5 kg PVA  
5% w/w stearamide (0.25 kg)  
5% w/w glycerol (0.25 kg)

Temperatures

10	Film				
	Blowing	Die	Work	Feed	
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	
15	211	211	207	202	
	Pressure	35-40 bar (3500-4000 kN/M <sup>2</sup> )			
	Torque	7.9-8.2 NM			
	RPM	303			

- 20      The quality of the film produced was good

Example 30Ingredients

- 25      5 kg PVA  
4% w/w stearamide (0.20 kg)  
5% w/w glycerol (0.25 kg)

30      Temperatures

	Film				
	Blowing	Die	Work	Feed	
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	
35	212	210	207	202	



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Pressure 45-50 bar (4500-5000 kN/M<sup>2</sup>)  
Torque 8-8.3 NM  
RPM 301

5

The quality was poor and the film produced was not commercial quality.

Example 31

10 Ingredients

5 kg PVA  
3% w/w stearamide (0.15 kg)  
5% w/w glycerol (0.25 kg)

15

Temperatures

	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
20	212	210	208	202

Pressure 48-50 bar (4800-5000 kN/M<sup>2</sup>)  
Torque 8.3-8.5 NM  
25 RPM 303

The film produced was poor quality.

Example 32

30

Ingredients

5 kg PVA  
2% w/w stearamide (0.10 kg)  
35 5% w/w glycerol (0.25 kg)

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Temperatures

	Film			
	Blowing	Die	Work	Feed
5	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	212	212	209	202
	Pressure	58-60 bar (5800-6000 kN/M <sup>2</sup> )		
10	Torque	9.1-9.4 NM		
	RPM	303		

The film produced was poor quality.

15 Example 33Ingredients

5 kg PVA

20 1% w/w stearamide (0.05 kg)

5% w/w glycerol (0.25 kg)

Temperatures

	Film			
	Blowing	Die	Work	Feed
25	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	212	215	210	202
30	Pressure	60-64 bar (6000-6400 kN/M <sup>2</sup> )		
	Torque	9.7-10.4 NM		
	RPM	303		

The quality produced was poor.

35

Example 34Ingredients

5     5 kg PVA  
      7.5% w/w stearamide (0.375 kg)

Temperatures

10	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	212	209	201	198
15	Pressure	40 bar (4000 kN/M <sup>2</sup> )		
	Torque	7.1-7.4 NM		

Very poor quality film produced.

20

Example 35Ingredients

25     5 kg PVA  
      5% w/w stearamide (0.25 kg)  
      4% w/w glycerol (0.20 kg)

Temperatures

30	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	214	219	211	199

35

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Torque 9.5-9.9 NM

The quality of the film produced was good.

5

Example 36

Ingredients

10 5 kg PVA  
5% w/w stearamide (0.25 kg)  
3% w/w glycerol (0.15 kg)

The quality of the film produced was poor.

15

Example 37

Ingredients

20 5 kg PVA  
5% w/w stearamide (0.25 kg)  
2% w/w glycerol (0.10 kg)

Very poor quality film produced.

25

The following examples detail the compounding temperatures resulting from processing the material under various different conditions at the pre-mixing stages.

30 Example 38

The PVA/stearamide and glycerol were heated to 140°C in the forced action blender.

35

- 25 -

Temperatures at compounding stage

		Film			
		Blowing	Die	Work	Feed
5		<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
		214	212	210	197
	Pressure	50-55 bar (5000-5500 kN/M <sup>2</sup> )			
10	Torque	8.1-8.6 NM			

The quality of the film produced was good.

Example 39

15

The mix was heated to 145°C during the pre-mix stage.

Temperatures at compounding stage

		Film			
		Blowing	Die	Work	Feed
20		<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
		213	213	211	197
25	Pressure	65 bar (6500 kN/M <sup>2</sup> )			
	Torque	8.6-8.9 NM			

The quality was borderline acceptable.

30 Example 40

The mix was heated to 150°C during the pre-mix stage.

35

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Temperatures at compounding stage

5	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	215	214	211	197

Pressure 65 bar (4000 kN/M<sup>2</sup>)

Torque 8.6-8.9 NM

10

The quality was borderline acceptable.

Example 41

15 The mix was heated to 160°C during the pre-mix stage.

Temperatures at compounding stage

20	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	213	209	210	198

Pressure 40 bar (4000 kN/M<sup>2</sup>)

25 Torque 7.1-7.3 NM

These parameters produced poor quality film.

Example 42

30

The mix was heated to 119°C during the pre-mix stage.

35

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Temperatures at compounding stage

5	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	214	215	211	197

Pressure 70 bar (7000 kN/M<sup>2</sup>)

Torque 9.0-9.4 NM

10

The quality of the film produced was good.

Example 43

15 The mix was heated to 117°C during the pre-mix stage.

Temperatures at compounding stage

20	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	216	215	211	197

Pressure 68-70 bar (6800-7000 kN/M<sup>2</sup>)

25 Torque 8.7-9.0 NM

The quality of the film produced was good.

Example 44

30

The mix was heated to 113°C during the pre-mix stage.

35

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Temperatures at compounding stage

5	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	213	215	211	196

Pressure 70-75 bar (7000-7500 kN/M<sup>2</sup>)

10 Torque 9.2-9.6 NM

The quality of the film produced was good.

Example 45

15 The mix was heated to 106°C during the pre-mix stage.

Temperatures at compounding stage

20	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	214	217	212	196

25 Pressure 75-80 bar (7500-8000 kN/M<sup>2</sup>)

Torque 9.6-10.0 NM

The quality of the film produced was good.

Example 46

30 The mix was heated to 100°C during the pre-mix stage.

35



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Temperatures at compounding stage

5	Film			
	Blowing	Die	Work	Feed
	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>	<u>Zone</u>
	213	213	209	195

Pressure 70-80 bar (7000-8000 kN/M<sup>2</sup>)

Torque 8.1-8.4 NM

10

The quality of the film produced was not commercial quality.

The improvements to biodegradable PVA plastics materials described herein can be summarised as follows:-

15

1. The PVA can be readily formed and worked to produce a non-laminated layer of PVA as a film or a shaped article.

2. Any or each surface of the film or article may be treated to render it water resistant.

20

3. This PVA plastics product, when ruptured and/or immersed in water will dissolve completely and will biodegrade to completion over a period of about 28 days excluding the phenoxy resin waterproofing agent which does not biodegrade.

25

4. All the components used in the manufacture of the PVA are foodgrade additives.

30 It will of course be understood that the invention is not limited to the specific details described herein, which are given by way of example only, and that various modifications and alterations are possible within the scope of the appended claims.

35

CLAIMS:

1. A method of manufacturing a biodegradable plastics material comprising mixing partially hydrolysed, water soluble polyvinyl alcohol (PVA) co-polymer with a plasticiser and stabiliser at a temperature in the range of between 106 to 140°C, whereby the resultant material can readily be worked by known processes and is suitable for the manufacture of water soluble and biodegradable articles.
2. A method according to Claim 1, wherein the method comprises the following steps:
  - a. mixing the stabiliser with the PVA; and
  - b. adding the plasticiser to the mixture of stabiliser and PVA and mixing at a temperature between 106 to 140°C.
3. A method according to Claim 1 or Claim 2, wherein after mixing the PVA, stabiliser and plasticiser, the method includes the steps of compounding the resultant product to produce a useable, commercial material wherein the compounding is carried out at a temperature in the range 195 - 225°C.
4. A method according to Claim 3, including the step of pelletising the resultant product to produce a useable, commercial pellet.
5. A method according to any preceding claim, wherein the method includes processing the plastics material further by blow moulding, cast extrusion, injection moulding or any other suitable plastics processing procedure.
6. A method according to any preceding claim, including mixing PVA and stabiliser in a forced action blender.
7. A method according to any preceding claim, characterised in that the

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stabiliser is included in an amount in the range of 4 to 6% w/w (weight of stearamide to weight of PVA).

5 8. A method according to any one of Claims 1 to 6, characterised in that the plasticiser is included in an amount in the range of 3 to 15% w/w (weight of plasticiser to weight of PVA).

10 9. A method according to any preceding claim, wherein the stabiliser is stearamide or a stearate.

10. A method according to any preceding claim, characterised in that the plasticiser comprises glycerol or glycerine solution or soya bean oil.

15 11. A method according to any one of the preceding claims characterised in that the mixing of PVA, stabiliser and plasticiser is carried out at a temperature in the range of 116 to 135°C.

20 12. A method according to any one of the preceding claims characterised in that the mixing of PVA, stabiliser and plasticiser is carried out at a temperature in the range of 123 to 129°C.

25 13. A method according to any of Claims 5 to 12 including the step of applying a waterproofing agent to at least a portion of the surface of the plastics material so that at least a portion of the material is rendered resistant to water to prevent premature dissolution of the product on contact with water.

30 14. A method according to Claim 13, wherein the waterproofing agent is phenoxy resin.

15. A biodegradable, plastics material produced by a method as claimed in any preceding claim.

35 16. An article produced by the method as claimed in any one of Claims 1 to 15, wherein the article is fully or substantially fully biodegradable.

17. An article produced by the method as claimed in any one of Claims 1 to 15, wherein the biodegrading of the article commences on contact of the article with water.

5

18. A method according to any one of the preceding claims, wherein PVA feedstock may be cold or hot soluble, partially hydrolysed PVA which is 70-85 wt % polyvinyl alcohol.

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1/1

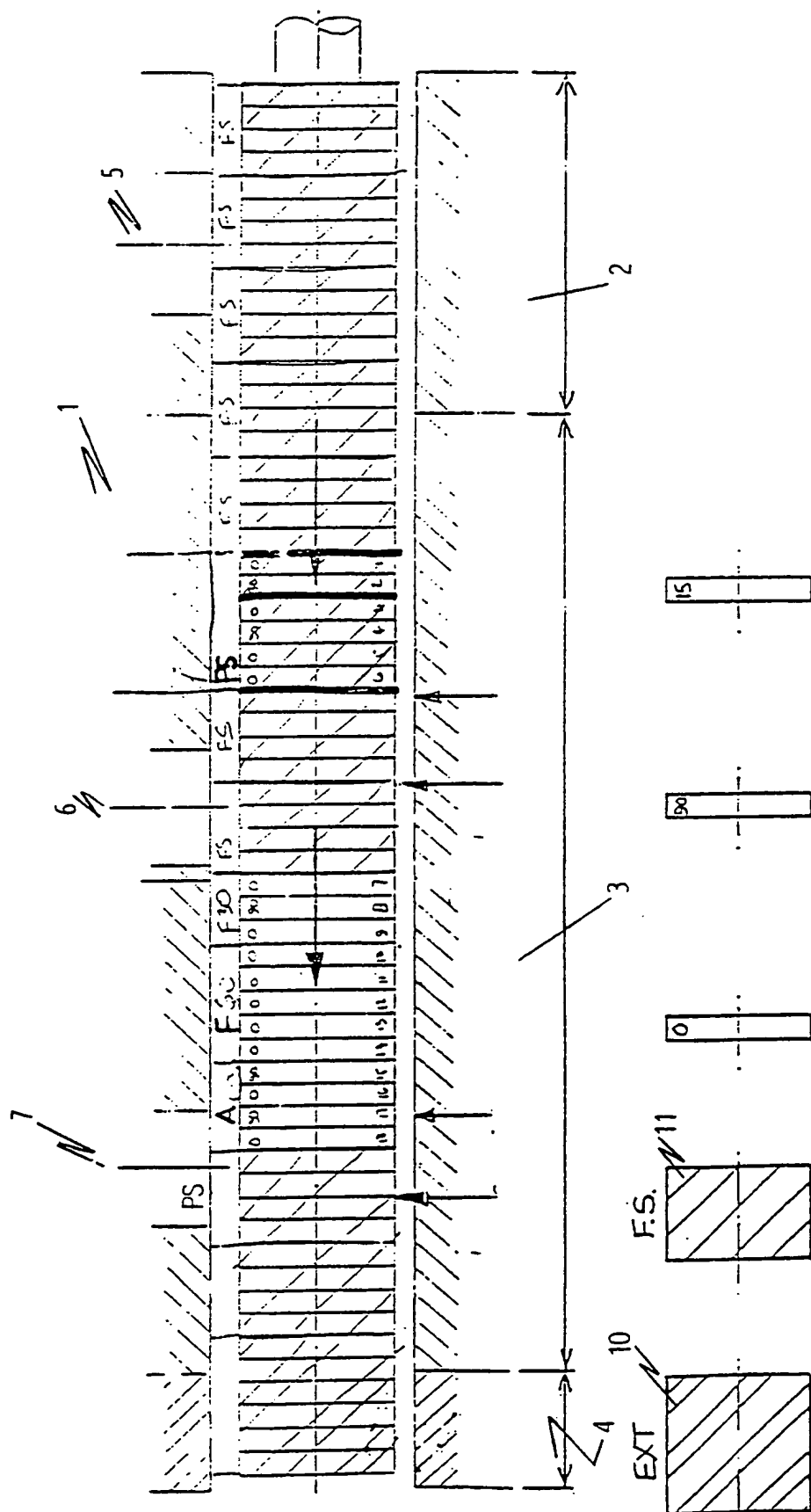


FIGURE 1

## INTERNATIONAL SEARCH REPORT

Application No

PC/IE 96/00060

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08L29/04 C08K5/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 635 545 A (AIR PROD & CHEM) 25 January 1995 see the whole document ---	1-18
Y	EP 0 004 587 A (HOECHST AG) 17 October 1979 see page 4, line 26 - page 5, line 16 see page 6, line 23 - line 33 see page 7, line 14 - line 23; claims; examples ---	1-18
Y	WO 92 01556 A (BHP PLASTICS LTD) 6 February 1992 cited in the application see page 10, line 2 - line 7; claims --- -/--	1-18

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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## INTERNATIONAL SEARCH REPORT

In Application No  
PCT/IE 96/00060

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5 322 866 A (MAYER JEAN M ET AL) 21 June 1994 see the whole document ---	1-18
A	WO 93 09171 A (NOVAMONT SPA) 13 May 1993 see claims; examples ---	1-12
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